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Carbon dioxide and methane in continental Europe: a climatology, and ^{222}Radon-based emission estimates

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ABSTRACT

4-year records of gas chromatographic carbon dioxide and methane observations from the continental mountain station Schauinsland in the Black Forest (Germany) are presented. These data are supplemented by continuous atmospheric ^{222}Radon observations. The raw data of CO_2 concentration show a large seasonal cycle of about 16 ppm with monthly mean wintertime enhancements up to 10 ppm higher and summer minima up to 5 ppm lower than the maritime background level in this latitude. These offsets are caused by regional and continental scale CO_2 sources and sinks. The mean CH_4 concentration at Schauinsland is 31 ppb higher than over the Atlantic ocean, due to the European continent acting as a net source of atmospheric CH_4 throughout the year. No significant seasonal cycle of methane has been observed. The long term CO_2 and CH_4 increase rates at Schauinsland are found to be similar to background stations in the northern hemisphere, namely 1.5 ppm CO_2 yr^{-1} and 8 ppb CH_4 yr^{-1}. On the time scale of hours and days, the wintertime concentrations of all three trace gases are highly correlated, the mean ratio of CH_4/CO_2 is 7.8 ± 1.0 ppb/ppm. The wintertime *monthly mean* concentration offsets relative to the maritime background level show a CH_4/CO_2 ratio of 6.5 ± 1.1 ppb/ppm, thus, not significantly different from the short term ratio. Using the wintertime regressions of CO_2 and ^{222}Radon respectively CH_4 and ^{222}Radon we estimate winter time CO_2 flux densities of 10.4 ± 4.3 mmol CO_2 m^{-2} h^{-1} (from monthly mean offsets) and 6.4 ± 2.5 mmol CO_2 m^{-2} h^{-1} (from short term fluctuations) and winter time methane flux densities of 0.066 ± 0.034 mmol CH_4 m^{-2} h^{-1} (from monthly mean offsets) and 0.057 ± 0.022 mmole CH_4 m^{-2} h^{-1} (from short term fluctuations). These flux estimates are in close agreement to CO_2 respectively CH_4 emission inventories reported for Germany from statistical data.

1. Introduction

The interpretation and assessment of greenhouse gas observations such as CO_2 and CH_4 concentrations at continental sites suffers from the large variability observed there on time scales of hours and days (Ciattaglia et al., 1987; Levin, 1987; Bakwin et al., 1995; Levin et al., 1995). However this variability, although largely caused by diurnal changes of the atmospheric transport conditions in the continental boundary layer (vertical temperature profile) also contains the signals from the continental sources which have to be investigated if we want to better quantify the global atmospheric budgets of these greenhouse gases. In the case of carbon dioxide, the

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source/sink situation is most complex as natural and anthropogenic sources are active *at the same time* as the assimilation sink. Concerning methane, the source/sink characteristics are much simpler as (1) the predominant sink by OH oxidation in the atmosphere can largely be neglected when dealing with time scales of hours or days. (2) The emissions from the ground level sources, which, in Western Europe are nearly 100% anthropogenic, namely releases from ruminants, waste deposits, natural gas leakages or coal mining (Thom et al., 1993), can be assumed as constant with time on the diurnal as well as on the seasonal time scale. Due to these different source/sink characteristics the *combined* interpretation of continuous parallel observations of CO_2 *and* CH_4 together with measurements of ^{222}Radon can be of considerable help to elucidate the causes of the observed variations.

In this study we present 4.5 years of continuous CO_2 and CH_4 observations from the German monitoring station Schauinsland in the Black Forest (48°N, 8°E, 1205 m a.s.l.). These measurements are supplemented by parallel observations of ^{222}Radon decay products performed at the same site. A climatology of all three gases is presented and CH_4/CO_2 ratios, characteristic for western European air masses, are calculated. This information may be very useful when interpreting trace gas records at background monitoring stations such as Izaña, Tenerife (Schmitt et al., 1988) or Alert, northern Canada (Worthy et al., 1994). In addition, an attempt is made to estimate CO_2 and CH_4 flux densities for the catchment area of the observation site, by using the parallel ^{222}Radon daughter activity measurements as a semi-quantitative transport tracer. Considering diurnal concentration variations, this catchment area is represented by the regional environment of up to several ten kilometers distance. When interpreting large scale air mass changes, the catchment area is probably as large as southwest Europe (or an area of several hundred kilometers diameter).

2. Sampling and analytical methods

2.1. Sampling site

The Schauinsland observatory is located in the Black Forest in southwest Germany at 47°55'N, 7°55'E (1205 m a.s.l.). This GAW (Global Atmosphere Watch) station is part of the Umweltbundesamt (UBA, Federal Environment Agency) monitoring network of the Federal Republic of Germany (Fig. 1). On the mountain ridge of the Schauinsland at an elevation of approximately 1000 m above the Rhine valley the station is housed isolated from local anthropogenic sources and surrounded by meadows and woods. In winter the area around the station is often covered with snow. During night, the Schauinsland is usually above the boundary layer inversion of the Rhine valley. During day time, and particularly in summer, it mostly lies within the boundary layer (Levin et al., 1995).

At the Schauinsland site, atmospheric CO_2 concentration is continuously measured by nondispersive infrared analysis (NDIR) since 1972 (Levin, 1987; Levin et al., 1995). In 1991 a new gas chromatographic system was built up for quasi-continuous measurement of CO_2, CH_4 (and N_2O). ^{222}Radon daughter measurements are made at the same location about 160 m apart from the UBA station at the measurement site of the Bundesamt für Strahlenschutz (BfS, Federal Radiation Protection Agency).

2.2. *CO_2 and CH_4 measurement technique*

Methane, carbon dioxide as well as nitrous oxide are measured simultaneously using an automated gas chromatograph (Sichromat 1–4, Siemens, Germany). Fig. 2 shows schematically the configuration of the GC system. It is equipped with a flame ionisation detector (FID), a Ni catalyst for conversion of carbon dioxide to methane and an electron capture detector (ECD) to determine N_2O. The system for N_2O separation and detection is being reconstructed at the moment, technical details and measurement results will be discussed elsewhere. The major features with emphasis on routine ambient air measurements of CO_2 and CH_4 are discussed here, for greater details see Schmidt (1992). The analytical system can be divided into three parts (see Fig. 2): (1) the air intake with a drying unit and an 8-port-sampling valve, (2) the chromatographic system and (3) the data acquisition and integration unit.

(1) Outside air is continuously flushed through a 5 m high glass inlet stack located about 2 m above the roof of the station and approx. 5 m

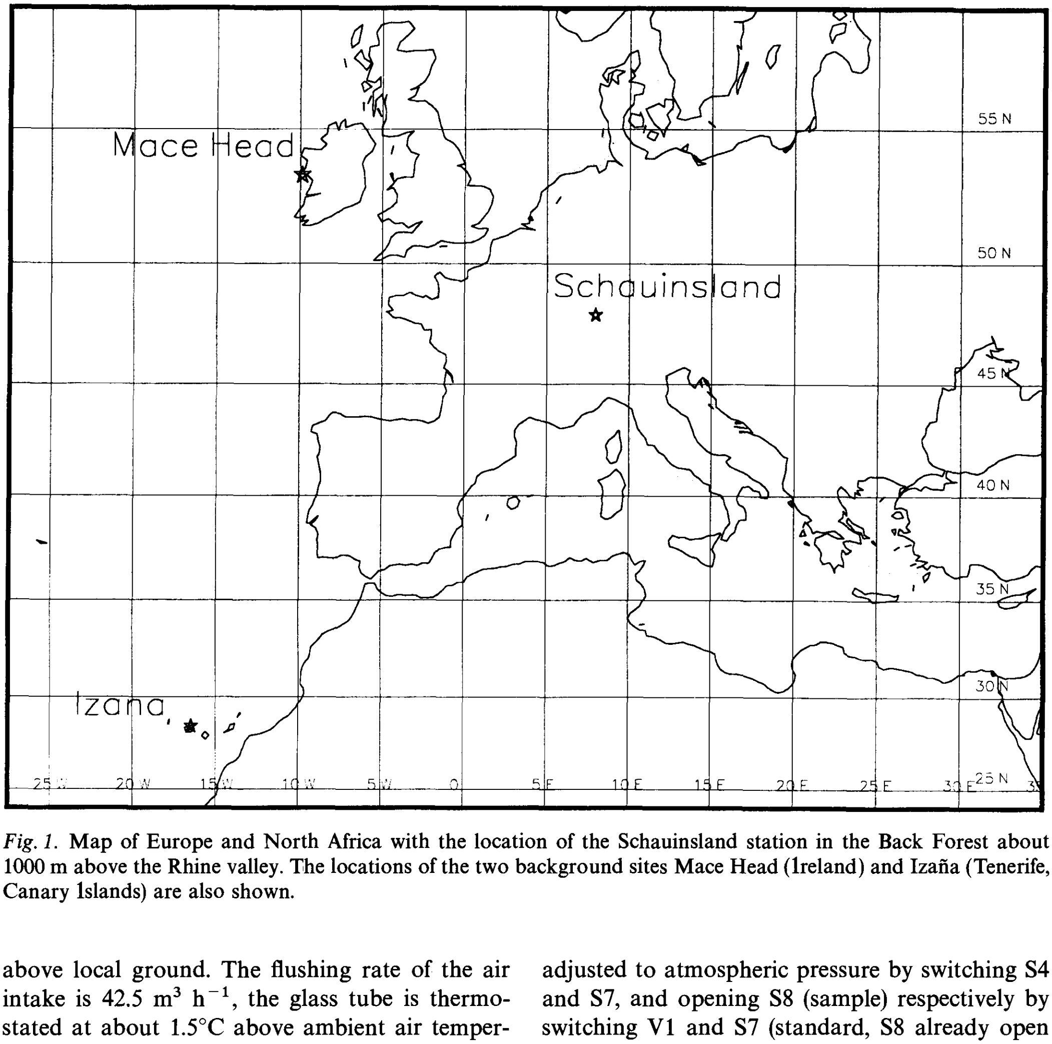

Fig. 1. Map of Europe and North Africa with the location of the Schauinsland station in the Back Forest about 1000 m above the Rhine valley. The locations of the two background sites Mace Head (Ireland) and Izaña (Tenerife, Canary Islands) are also shown.

above local ground. The flushing rate of the air intake is 42.5 $m^3 h^{-1}$, the glass tube is thermostated at about 1.5°C above ambient air temperature to prevent water vapor condensation. From this main air intake the sample air is collected with a membrane pump (Miniport N06 KN18, Neuberger, Germany). Before entering the 8-port sampling valve V1 the air is passed through a drying unit. The automated sampling valve (V1) alternates between ambient air and standard gas. To prevent contamination, the pump is located at the end of the line, sucking the sample through the sample loops at the 10-port injection valve V2 and the solenoid S4. In contrast to the air sample, which is flushed through the sample loops at *under-pressure*, the standard gas flushes through the sample loops at *over-pressure* (V1, V2, solenoid S4 and S8). In both cases the sample loops are adjusted to atmospheric pressure by switching S4 and S7, and opening S8 (sample) respectively by switching V1 and S7 (standard, S8 already open during flushing).

(2) The chromatographic system consists of the 10-port injection valve (V2) with two sample loops, one for CO_2/CH_4 (3 ml) and one for N_2O (5 ml). The chromatographic columns as well as the sample loops are thermostated in the GC oven at a temperature of 40 ± 0.1°C. A stainless steel column (1.2 mm inner diameter, 11 m long, packed with HaySep S) is applied for separation of CH_4 and CO_2. Ultra pure nitrogen (>99.999%) at a flow rate of 2.2 L h^{-1} is used as carrier gas; the retention times are 4.5 min for CH_4 and 8.7 min for CO_2, respectively. To convert carbon dioxide to methane for detection at the FID we use a Ni catalyst which is directly mounted in the glass

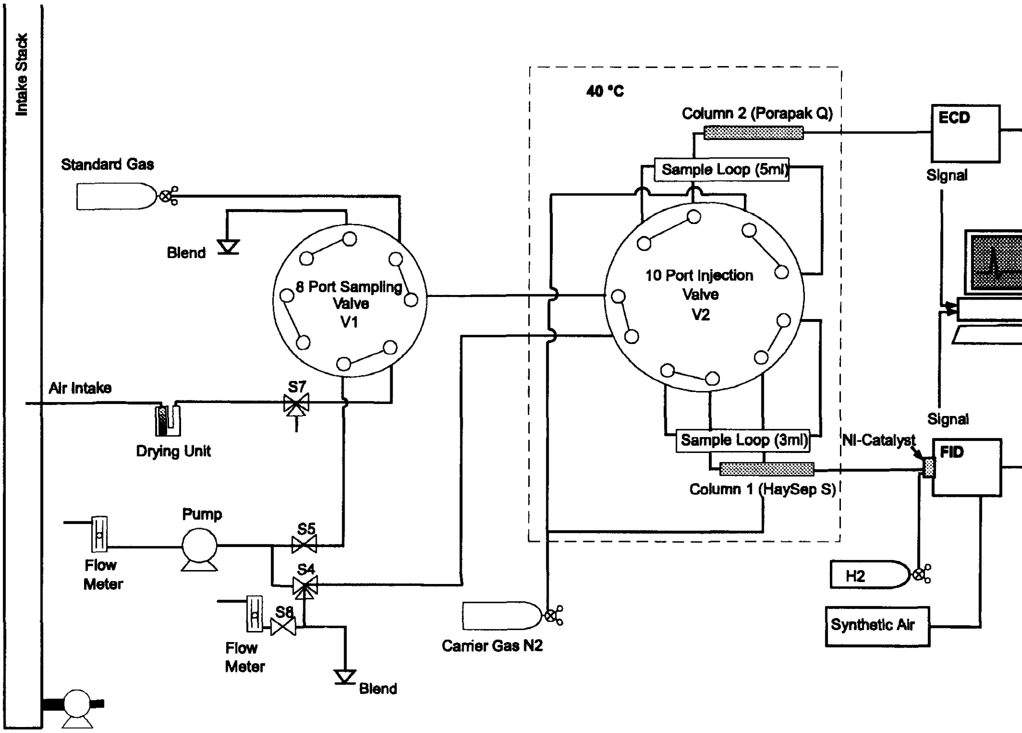

Fig. 2. Schematics of the gas chromatographic system. The components located in the thermostated GC oven are framed by dashed lines. The measurement system for all three components, CO_2, CH_4 and N_2O is shown for completeness.

tube of the FID jet, support gases for the FID are ultra pure H_2 (>99.999%) and purified air (TJ 36, J.U.M. Engineering).

(3) Data acquisition and integration unit: Valve switching and thermostating of the oven and the detectors are performed by the controlling system steering gear of the GC. The FID and ECD signals are recorded and integrated by a personal computer (PC). Concentrations of standard gas and ambient air are calculated from the peak areas of the chromatogram. One measurement cycle with one standard gas and one ambient air injection is repeated every half hour providing 48 ambient air measurements per day.

Methane concentrations are referenced to standard gases calibrated by NOAA/CMDL in 1995. The CO_2 data are reported in the WMO 1987 mole fraction scale, calibrated by Scripps Institution of Oceanography in 1989. As mentioned above, at the Schauinsland site CO_2 concentration is continuously measured also by NDIR (Levin et al., 1995). Hence the comparison of the different methods applied (GC and NDIR) provide a good opportunity to identify possible systematic errors as will be discussed in the following paragraph.

2.3. *Comparison of CO_2 measurements by NDIR and GC*

When comparing the CO_2 concentration measurements made by GC with the long established measurement by NDIR we have to keep in mind that the NDIR system provides real half hourly mean values whereas with the GC system only one single spot measurement of ambient CO_2 concentration is made every half hour. Especially during periods with quickly changing atmospheric CO_2 concentrations we, therefore, should expect large deviations between the two systems for single data points. In the long term average the difference should, however, be zero. In the period of June 1992 to February 1995 we observed systematic offsets between the continuous NDIR and the gas chromatographic CO_2 measurements which finally turned out to be caused by (1) ineffective drying of the air sample and (2) uncomplete adjustment of the sample loops to barometric pressure. Both gases, CO_2 as well as CH_4 are effected by these errors.

(1) Since installation of the GC system in 1991 three different procedures have been applied to dry the sample gas before passing the chromatographic columns. From June 91 to May 93, the sample gas was dried with $Mg(ClO_4)_2$. In the following period, until May 94, no drying has been applied, and the data were corrected on the basis of air humidity and temperature measurements. Since June 94 we used a cryogenic trap to dry the sample air before injection. Incomplete drying of the air sample with $Mg(ClO_4)_2$ in the period from June 1992 until May 1993 was identified through a systematic difference between GC and NDIR CO_2 concentrations, which was strongly dependent on absolute humidity. We were, thus, in principle able to correct our data on the basis of the monthly mean CO_2 deviations from the NDIR measurement. For the final correction applied here we did, however, only use two different correction factors F, as individual monthly corrections would not have improved the data quality, respectively, the sigma of the concentration difference between the two systems after correction: for summer, June to September, $F = 1.0072 \pm 0.0012$, and for the rest of the year, $F = 1.0017 \pm 0.0004$ (*cf.* Table 1).

(2) The cause of the uncomplete pressure equilibration in the sample loops was replacement of the 10 port injection valve (V2) in August 1992. At that time also the 2-way solenoid S7 had erroneously been removed. S8 was always closed during pressure equilibration of the sample, and adjustment to barometric pressure was not fast enough, and only towards the intake stack which is at a small permanent under-pressure. Due to this error, the GC measurements showed 0.39 ± 0.02 % lower CO_2 concentrations than the NDIR measurements, respectively. In March 1995 the GC system was repaired and from there on the offset between GC and NDIR is negligible (<0.03 %).

For the total 4.5-year period of July 1991 to December 1995. Table 1 summarises the correction factors applied, as well as the mean standard deviation (1) of the difference between GC and NDIR CO_2 measurement after correction. This standard deviation is the maximum measurement error for CO_2 (and CH_4) analysis with the GC system in the different periods. It includes also the precision of the NDIR measurement (see below). The reproducibility of the CO_2 measurement of a standard gas with the GC system is ± 0.6 ppm (1σ). For methane, the reproducibility is ± 4 ppb (1σ). The relatively large standard deviation of the CO_2 difference between GC and NDIR in the period of June 1991 to September 1992 is also caused by unstable NDIR measurements with the Ultramat 3 instrument (Siemens, Germany). The Ultramat 3 has been replaced by an URAS 3E (Hartmann & Braun, Germany) instrument on 21 September, 1992. Since March 1995, the mean standard deviation of the difference between GC and NDIR CO_2 measurement of ± 1.0 ppm is

Table 1. *Correction factors applied to the GC CO_2 and CH_4 concentrations and standard deviation of the difference between NDIR and GC CO_2 concentration after correction*

Begin	End	Dryer correction	Pressure correction	1σ of ΔCO_2 (ppm)
June 1991	February 1992	–	–	2.1
March 1992	May 1992	no data		
June 1992	July 1992	1.0072 ± 0.0012	–	2.3
August 1992	September 1992	1.0072 ± 0.0012	1.0039 ± 0.0002	2.3
October 1992	May 1993	1.0017 ± 0.0004	1.0039 ± 0.0002	1.8
June 1993	February 1995	–	1.0039 ± 0.0002	1.6
March 1995	December 1995	–	–	1.0

nearly a factor of two larger than the measurement precision, and is also partly caused by the fact that the GC measurement is only a spot analysis of ambient concentration whereas the NDIR values represent real half hourly means.

The additional uncertainty of our measurements through the water vapor and pressure adjustment corrections, respectively the standard deviations between GC and NDIR for the corrected CO_2 concentrations, are still small if compared to the observed variabilities at the measurement site. They have, thus, no significant effect on any quantitative estimate deduced from the CO_2 and CH_4 records.

2.4. *Measurement technique for the atmospheric ^{222}Radon daughter activity*

Under most meteorological conditions, the short-lived ^{222}Radon daughters are in secular radioactive equilibrium with atmospheric ^{222}Radon, hence the atmospheric ^{222}Radon (gas) activity can be determined via its short-lived aerosol-attached daughter activity. At the Schauinsland (BfS) station, ^{222}Radon is, therefore, measured with the so-called filter method: Outside air is continuously pumped through a filter, where the ^{222}Radon daughters which are attached to aerosols, are quantitatively collected. The α-decay of the ^{222}Radon daughters ^{218}Po ($\alpha_E = 6.0$ MeV) and ^{214}Po ($\alpha_E = 7.7$ MeV) is measured in situ, and the atmospheric ^{222}Radon (gas) activity is then calculated from the ^{222}Radon daughter activity assuming radioactive equilibrium. The maximum time resolution of ^{222}Radon measurements with the filter method is 0.5 to 1 hour, due to the time lag of the radon daughter activity on the filter to ^{222}Radon changes in ambient air activity. The measurement technique is described in detail by Stockburger and Sittkus (1966).

3. Results and discussion

3.1. *Typical concentration records observed at the Schauinsland station*

An example of the complex information hidden in the raw data obtained at Schauinsland mountain station is shown in Figs. 3, 4. A typical winter situation is represented by the week from 9–16 February, 1994. During the first half of this period winds are coming from westerly directions with trace gas concentrations close to maritime background levels. For comparison, the maritime concentration records of CO_2 and CH_4 as represented by measurements obtained by NOAA/CMDL (Conway et al., 1994; Dlugokencky et al., 1994) for Mace Head and Izaña (Tenerife) station (see Subsection 3.2.) are given as dashed lines in Figure 3a, c. The ^{222}Radon level of 1–2 Bq m^{-3} points to a residence time of the air mass over the continent well below two days. On 11 February, winds change from west over north to easterly directions, with longer transport times of the air over the continent. Wind speeds are persistently high; however, the increasing large scale continental source influence leads to slowly rising CO_2 and CH_4 concentrations, as well as rising ^{222}Radon activity. On 15 February, the wind slows down and the Schauinsland station is now influenced by a local wind regime with frequently changing directions. This leads to a fast increase of all three trace gases to maximum concentrations on February 13–14. It is interesting to note that CO_2 and CH_4 show a very clear parallel behaviour whereas ^{222}Radon, although roughly in phase, also shows unique singularities, for example, a very high peak around noon on February 14 (see also Subsection 3.3.).

A typical summer, respectively autumn, situation is represented by the week of September 19–25, 1994 (Figure 4). CH_4 and ^{222}Radon vary strictly in parallel as is the case during winter whereas CO_2 concentrations are rather anticorrelated. For all three gases large diurnal variations are observed, particulary in the second half of the week. During night, methane and CO_2 concentrations are often close to maritime background values: downslope winds transport clean air from higher atmospheric levels to the sampling site. During the day, maxima of CH_4 and ^{222}Radon are observed, which are caused by transport of (night time) soil-born emissions from the Rhine valley to the mountain station. These maxima are associated to CO_2 minima caused by net plant assimilation during daytime, when upslope winds bring air to the sampling station, which has been in close contact with ground level vegetation on the slopes of the mountain. CO_2 concentration during day then often falls below the maritime

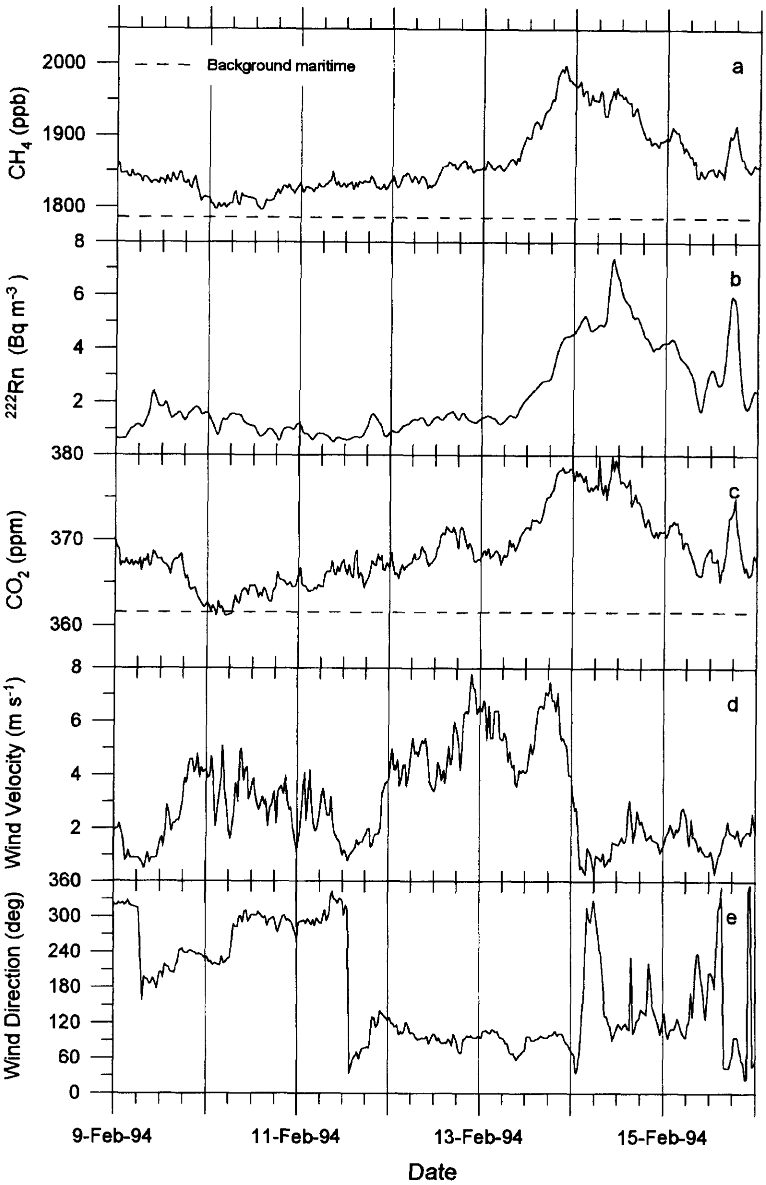

Fig. 3. Time series of half hourly measurements of CH_4 (a) and CO_2 (c) concentration, ^{222}Radon activity (b), wind velocity (d) and wind direction (e) at Schauinsland from 9–16 February, 1994. The dashed lines represent maritime background concentrations derived from the NOAA/CMDL network (see text and Fig. 5). In this typical week in winter, all three trace gas concentrations are strikingly correlated.

background level. This diurnal circulation pattern with upslope winds during the day and downslope winds during night is typical for mountain stations during summer (Levin, 1987; Schmitt et al., 1988; Levin et al., 1995). The correlations between methane, ^{222}Radon and carbon dioxide will be used to estimate CO_2 and CH_4 fluxes for the catchment area of the sampling site (see Subsection 3.4.).

3.2. *Long-term trend and seasonal cycles of CO_2, CH_4 and ^{222}Radon*

The long-term features as well as the characteristics of the seasonal and diurnal CO_2 concentration variations at Schauinsland station have been investigated by Levin et al. (1995). In the present study, we want to examine the combined records of CO_2 and CH_4 in terms of local and regional natural and anthropogenic sources and sinks of these gases. In order to estimate the source influence over the European continent, we first have to determine the maritime background concentration of the air before it reaches the continent.

Within the cooperative network of NOAA/CMDL (Conway et al., 1994; Dlugokencky et al., 1994) weekly flask samples are collected from the Atlantic stations Mace Head (Ireland, 53°N, 10°W, 25 m a.s.l.) and Izaña (Tenerife, Canary Islands, 28°N, 16°W, 2367 m a.s.l.) and analysed for CO_2 and CH_4. We used these data and calculated *latitude weighted* monthly means for 48°N from Izaña and Mace Head observations by weighing the Mace Head surface data four times, and the high altitude Izaña data only once (for the locations of these background sites, see Fig. 1). This weighing procedure is arbitrary, however, including Izaña in the maritime background concentration for Schauinsland also accounts for the decrease of amplitude with height. From the NOAA/CMDL network, monthly data have been published for CH_4 and CO_2 until the end of 1993. To extrapolate the *maritime background* curve until end of 1995 for CO_2 the mean seasonality from 1991 to 1993 was used and an increasing trend of 1.5 ppm yr^{-1} which corresponds to the mean long-term trend of CO_2 in the northern hemisphere (Conway et al., 1994). An equivalent procedure was used to derive CH_4 background values for 1994–1995, here we used an increase rate of 8 ppb yr^{-1} which is the mean increase at Schauinsland during our observations and agrees well with other recent northern hemispheric records (Dlugokencky et al., 1994).

Fig. 5a shows the monthly mean methane concentration at Schauinsland in comparison to this maritime background. With one exception (November 1992), as expected, methane is always higher at Schauinsland station than over the Atlantic ocean. The mean offset from July 1991–December 1995 is 31 ppb (Fig. 5d) with a month to month variability (1σ) of ± 18 ppb. Although the methane concentration itself does not show a seasonal cycle at Schauinsland, in some years, the continental CH_4 offset seems to be lower during the winter months (1992–93 and 1994–95) if compared to the rest of the year. The almost solely anthropogenic methane sources like ruminants, leakages from natural gas supply, coal mining and waste deposits (Thom et al., 1993), responsible for this offset, are, however, not likely to vary with season. On the other hand, also ^{222}Radon shows significantly lower values during the winter months November–February than during the rest of the year. Also the ^{222}Radon emanation rate, at least from the sandy soils in the Rhine valley, is more or less constant over the year. Seasonal variations of the ^{222}Radon flux from western European soils have only been observed from loamy and clay soils (Dörr and Münnich, 1990; Schüßler, 1996). Here an about 25% lower flux is observed in winter than in summer time, which is most probably caused by higher soil humidity in winter, and, thus, a smaller diffusion coefficient of ^{222}Radon from the soil air into the atmosphere. But, the lower ^{222}Radon concentrations at Schauinsland in winter can also be caused by reduced vertical mixing in the continental boundary layer: During mid winter, solar irradiation is lowest and vertical convection in the lower troposphere is very weak. The Schauinsland station at about 1000 m above the Rhine valley is often decoupled from the ground level (pollutant) sources. As a consequence, the influence of ^{222}Radon and, likewise, methane emissions from the valley at the mountain site is lower during winter than during summer when source methane and ^{222}Radon are effectively transported to higher atmospheric levels by convective processes (compare Fig. 4).

Atmospheric CO_2 shows a large seasonal cycle with a peak-to-peak amplitude of about 16 ppm and maximum values during late winter. The winter monthly mean values are up to 10 ppm higher than observed at the maritime sites which is due to the continents acting as a net source of natural (soil and root respiration) and anthropogenic (fossil fuel) CO_2. There is a significant phase shift in the spring and early summer draw down of CO_2 concentration between the continental record and the maritime background, with Schauinsland decreasing earlier. The monthly

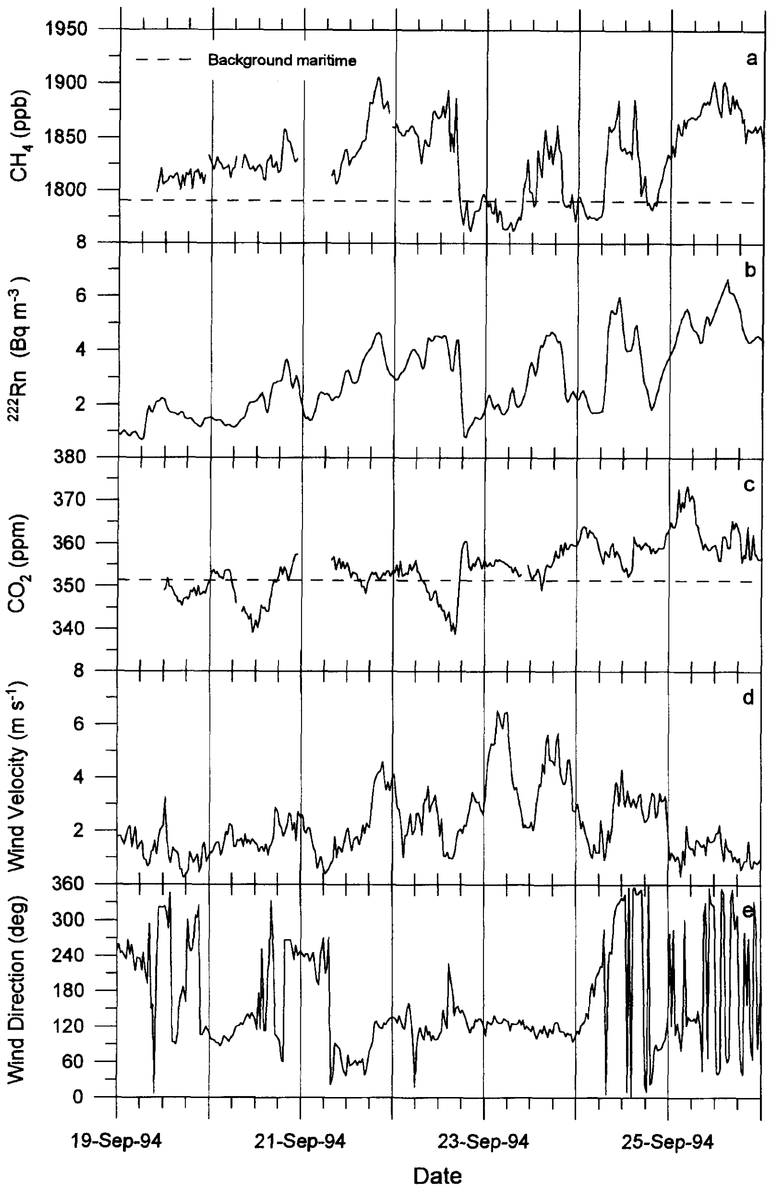

Fig. 4. Same as Fig. 3 but for a typical week in summer/autumn. During this time of the year, only CH_4 and ^{222}Radon, having a *net* continental source, are correlated whereas CO_2, during daytime and low winds, shows strong depletions below background concentration due to plant CO_2 uptake.

mean offset between Schauinsland and the maritime background is given in Fig. 5e. A significant negative offset due to CO_2 uptake by local or large scale vegetation is observed during the summer months.

Levin et al. (1995) proposed a selection procedure for the Schauinsland CO_2 concentrations to remove locally influenced data from the large scale features and to obtain a record representative for a larger area over the European continent. They

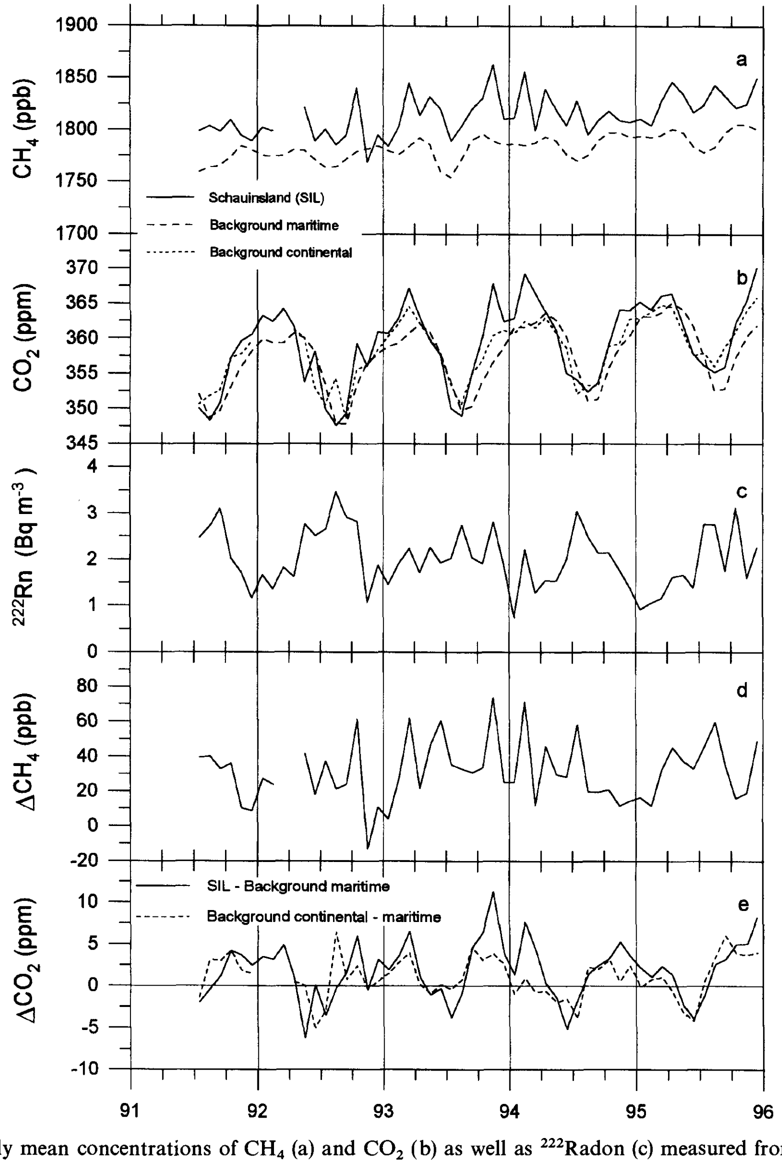

Fig. 5. Monthly mean concentrations of CH_4 (a) and CO_2 (b) as well as ^{222}Radon (c) measured from July 1991 to December 1995 (solid lines). The long dashed lines in (a) and (b) represent the *maritime* background concentrations derived from the NOAA/CMDL network (see text). The selected *continental* background concentrations for CO_2 are given as short dashed line in (b). The methane concentration at Schauinsland does not show a seasonal cycle but a mean offset of 31 ppb compared to maritime background levels (d). Atmospheric CO_2 shows a large seasonal concentration cycle. The offset to maritime and continental background concentrations is positive during winter and negative during summer (e).

used local wind speed and accepted only half hourly CO_2 concentration values as representative when the wind speed was higher than 2.5 m sec^{-1} in summer and higher than 3.5 m sec^{-1} in winter. Monthly mean concentration values selected in the same way, but, in addition, accepting only night-time values, are given in Fig. 5b for comparison. The offset of this *continental* background to the *maritime* background concentrations is shown in Fig. 5e as dashed line. The seasonality of the CO_2 offset—positive in winter and negative in summer—is still observed and must be interpreted as the large scale effect of CO_2 sources and sinks in Europe. It is interesting to note that this large scale continental offset is not symmetrical: the yearly mean offset is positive. This is partly due to the European continent acting as a *net* source of CO_2 (anthropogenic emissions) but partly also due to an asymmetrical effect of the winter time CO_2 pile up in the shallow planetary boundary layer leading to enhanced winter concentrations, particularly over the continents (compare Denning et al., 1995).

From Fig. 5d, e it seems as if in the winter half year (November to February) at least the peak values of the CO_2 and CH_4 offsets are correlated (Fig. 6a). However, there exists no clear source-related causality of this correlation—we rather interprete it as caused by the meteorological transport parameters influencing atmospheric concentrations of all soil-borne trace gases in a common way. This is underlined by the significant correlation in winter of ^{222}Radon with CO_2 and CH_4 (Fig. 6b, c). In summer, the monthly mean continental CH_4 offset is, however, not correlated with ^{222}Radon (Fig. 6d), although on the shorter time scale of hours and days, CH_4 and ^{222}Radon concentration changes are often also highly correlated in summer (see Table 2).

3.3. Diurnal cycles of CO_2, CH_4 and ^{222}Radon

Fig. 7 shows the mean *diurnal* cycles at Schauinsland for winter (January), spring (April), summer (July), and autumn (October) over the three year period of July 1992 to June 1995 where consecutive data of all three components CO_2, CH_4, and ^{222}Radon exist. Smallest diurnal variations are observed in winter when atmospheric convection is low. Little convection is probably

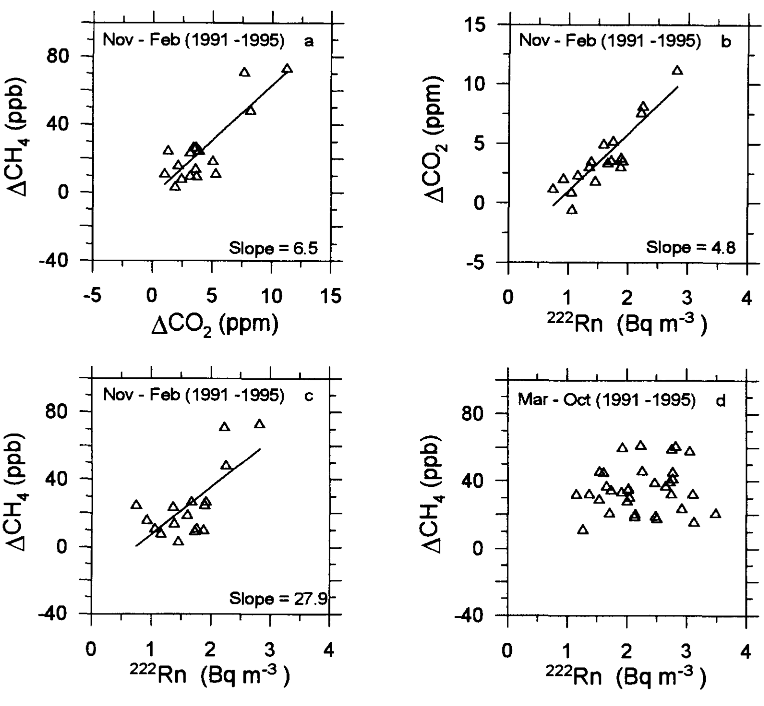

Fig. 6. Scatter plot of the winter monthly mean CH_4 and CO_2 offset (a), the winter monthly mean CO_2 offset and the monthly mean ^{222}Radon activity (b) as well as the monthly mean CH_4 offset and the ^{222}Radon activity in winter (c) and in summer (d). The straight lines are linear regression fits with slopes of: (a) 6.5 ± 1.1 (ppb CH_4)/(ppm CO_2), $R^2 = 0.7$; (b) 4.8 ± 0.6 (ppm CO_2)/(Bq m^{-3} ^{222}Rn), $R^2 = 0.8$; (c) 27.9 ± 7.2 (ppb CH_4)/(Bq m^{-3} ^{222}Rn), $R^2 = 0.5$. Monthly mean CH_4 offset and ^{222}Radon activity do not show a significant correlation from March to October.

Table 2. *Monthly mean slopes of the regression lines from the correlation of half hourly values*

	91/92		92/93		93/94		94/95		Mean
	CH_4/CO_2 (ppb/ppm)	R^2	CH_4/CO_2 (ppb/ppm)	R^2	CH_4/CO_2 (ppb/ppm)	R^2	CH_4/CO_2 (ppb/ppm)	R^2	$R^2>0.25$
Nov	7.1	0.88	6.6	0.50	7.0	0.95	4.8	0.62	6.4 ± 1.1
Dec	7.5	0.74	8.4	0.92	7.4	0.81	8.6	0.92	8.0 ± 0.6
Jan	8.0	0.91	8.7	0.74	8.0	0.82	7.1	0.83	8.0 ± 0.7
Feb	9.9	0.88	7.9	0.69	8.8	0.91	8.7	0.65	8.8 ± 0.8
	$CO_2/^{222}Rn$ (ppm/ Bq m^{-3})	R^2	$CO_2/^{222}Rn$ (ppm/ Bq m^{-3})	R^2	$CO_2/^{222}Rn$ (ppm/ Bq m^{-3})	R^2	$CO_2/^{222}Rn$ (ppm/ Bq m^{-3})	R^2	$R^2>0.25$
Nov	(2.2	0.16)	2.4	0.41	3.5	0.40	3.1	0.30	3.0 ± 0.6
Dec	(1.8	0.19)	(1.0	0.12)	2.5	0.82	2.4	0.57	2.5 ± 0.1
Jan	3.4	0.55	(1.3	0.19)	1.9	0.38	3.2	0.49	2.8 ± 0.8
Feb	1.8	0.43	2.5	0.39	3.5	0.37	(1.2	0.14)	2.6 ± 0.9
	$CH_4/^{222}Rn$ (ppb/ Bq m^{-3})	R^2	$CH_4/^{222}Rn$ (ppb/ Bq m^{-3})	R^2	$CH_4/^{222}Rn$ (ppb/ Bq m^{-3})	R^2	$CH_4/^{222}Rn$ (ppb/ Bq m^{-3})	R^2	$R^2>0.25$
Aug	15.6	0.26	(0.9	0.02)	16.5	0.33	(7.5	0.11)	16.1 ± 0.6
Sep	12.1	0.26	11.0	0.41	(13.2	0.16)	25.3	0.61	16.1 ± 8.0
Oct	17.1	0.54	22.3	0.56	(21.7	0.23)	(5.0	0.03)	19.7 ± 3.7
Nov	(18.5	0.20)	(10.7	0.12)	26.4	0.41	(14.8	0.19)	26.4
Dec	(14.4	0.19)	20.8	0.38	22.4	0.73	21.9	0.60	21.7 ± 0.8
Jan	28.3	0.54	(10.2	0.13)	17.9	0.46	19.5	0.28	21.9 ± 5.6
Feb	21.7	0.49	(10.6	0.20)	30.6	0.38	(14.7	0.19)	26.2 ± 6.3
Mar	–	–	24.3	0.50	(13.2	0.17)	25.6	0.5	25.0 ± 0.9
Apr	–	–	(6.8	0.05)	25.3	0.40	4.5	0.28	24.9 ± 0.6
May	15.2	0.35	23.7	0.33	(6.5	0.01)	(7.9	0.06)	19.5 ± 6.0
Jun	(5.2	0.01)	(9.9	0.02)	15.8	0.37	(−4.8	0.01)	15.8
Jul	(3.2	0.01)	(10.6	0.18)	22.4	0.27	(14.3	0.24)	22.4

Mean slopes have been calculated only from those months where the correlation coefficient R^2 was larger than 0.25.

also mainly responsible for the very low mean ^{222}Radon level of only 1 Bq m^{-3} at Schauinsland in January. A small concentration bump occurs in all three components even in high winter in the late afternoon as a result of upward mixing of ground level pollutants from the Rhine valley sources. This general diurnal behaviour with a concentration increase between 10:00 and 14:00 hrs, namely around noon is a general feature in the CH_4 and ^{222}Radon diurnal cycles throughout the year. The concentration increases are earliest and largest in July when vertical convection processes during the day are very strong and, correspondingly, also night time inversions in the valley are strong with large concentration pile-ups under the inversion layer (Levin, 1987).

For CO_2 concentration at the Schauinsland, the situation is different due to the assimilation sink depleting CO_2 concentrations during the day in the northern hemispheric growing season (April to October). The day time concentration draw down is largest in July where a steep concentration decrease occurs early in the morning after sunrise. Also in CO_2 in July we observe a small concentration bump around noon, coincident with the CH_4 and ^{222}Radon bumps which is a remnant of the night time concentration pile-up in the valley.

In Subsection 3.2. and Fig. 6 *monthly mean* concentration *offsets* have been correlated with ^{222}Radon, and the mean $\Delta CH_4/\Delta CO_2$ ratio has been calculated for the winter months (November to February) when the CO_2 assimilation sink is neglibible. These offsets are generated by emissions from regional sources (e.g., from the near-by Rhine valley), but also contain contributions from more distant sources active on the transport way of the

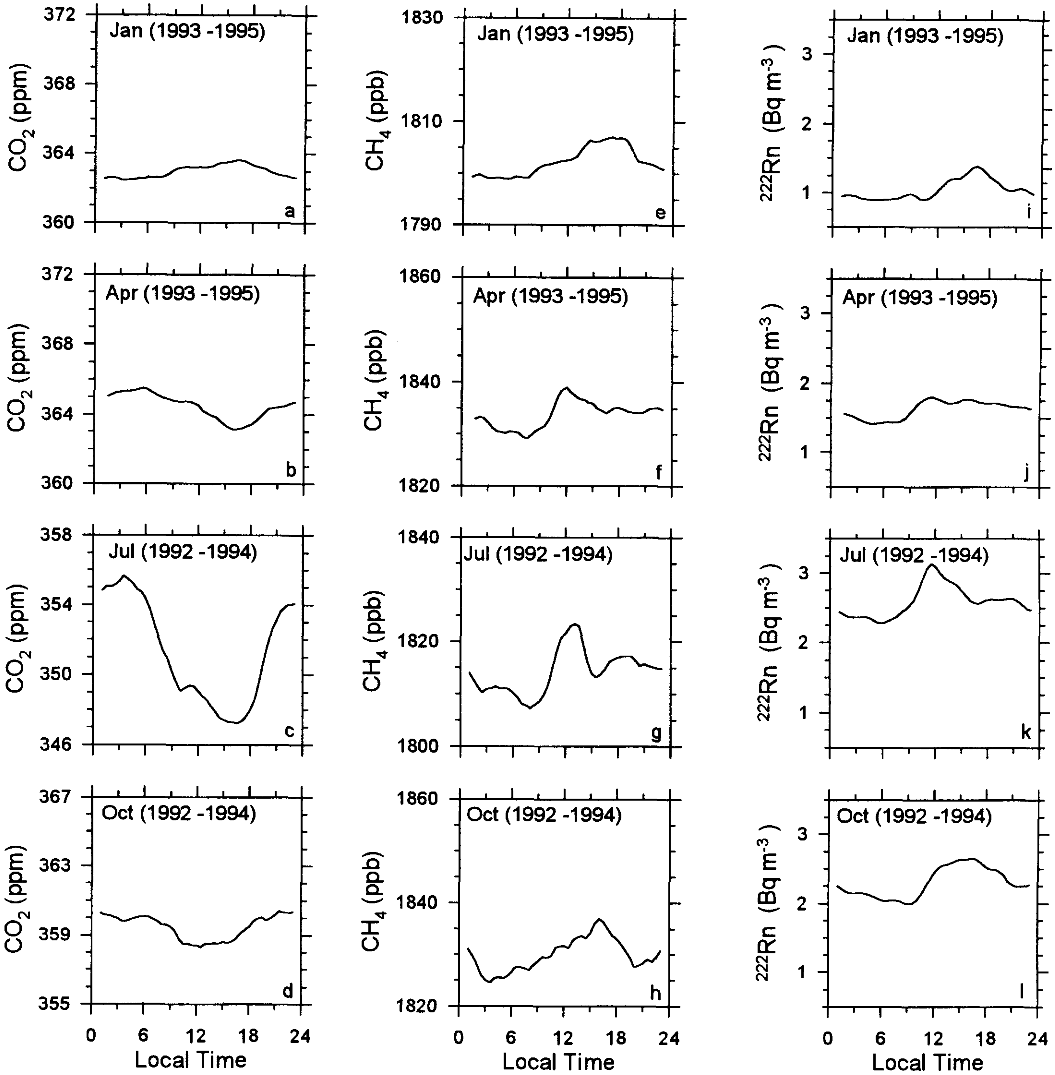

Fig. 7. Mean diurnal cycles for winter, spring, summer and autumn of CO_2 and CH_4 concentration and of ^{222}Radon activity for the years 1992 to 1995. CH_4 and ^{222}Radon show peak concentration values around local noon (10:00 to 14:00 hours) caused by convective transport of Rhine valley air to the mountain site. CO_2 concentration in summer is influenced by plant assimilation during daytime.

respective air parcel from the coast to the observational site (several hundred km). The *diurnal* variability of the trace gas concentrations is larger by a factor of 2 to 3 if compared to the *seasonal* variability of the respective offsets and is mainly caused by diurnal changes of the vertical diffusion coefficient in the boundary layer. The correlation of half hourly values, thus, provides information mainly on the regional source mix and flux densities (see Subsection 3.4.) of the Rhine valley sources.

Fig. 8 shows the correlation of CH_4 and CO_2 (a-d), CO_2 and ^{222}Radon (e-h) as well as CH_4 and ^{222}Radon (i-l) for the winter months November 1994 to February 1995. The slopes of the regression lines for all four winter periods of observa-

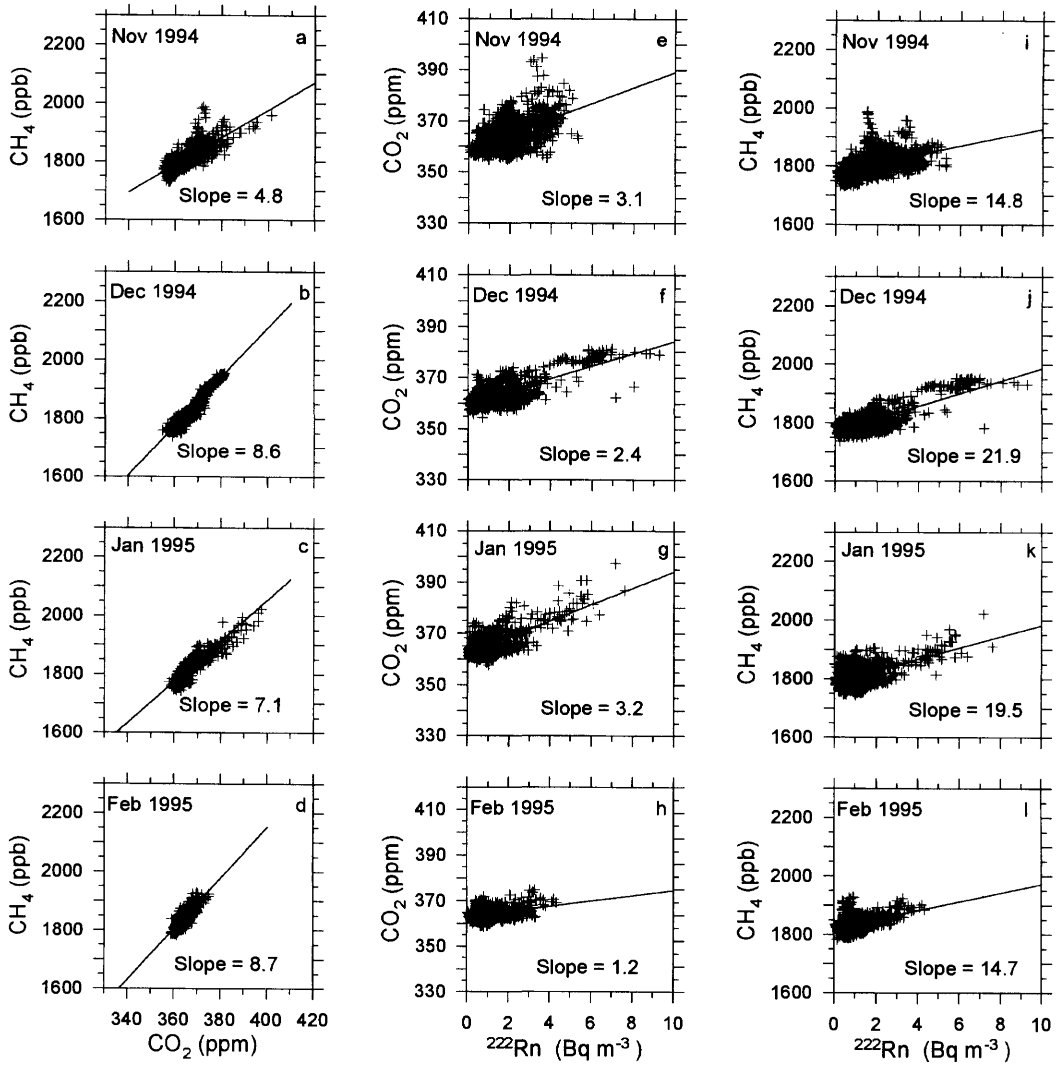

Fig. 8. Scatter plot of all half hourly concentration values of CH_4 and CO_2 (a–d), CO_2 and ^{222}Radon (e–h) as well as CH_4 and ^{222}Radon (i-l) during winter 1994/95. The straight lines are linear regression fits through all data. The slopes and their standard deviations and the correlation coefficients are summarized in Table 2. Whereas CH_4 and CO_2 during December to February fall onto a single line, CH_4 respectively CO_2 and ^{222}Radon more often show bimodal correlations.

tions are given in Table 2 together with the regression coefficients. Mean values are calculated from those months where significant correlations have been found ($R^2 > 0.25$). In all four years there exists an excellent correlation between CO_2 and CH_4 concentrations ($R^2 > 0.5$). Obviously, the distributions of anthropogenic CO_2 and CH_4 sources in the Rhine valley which is the main source region for the short-term increases observed at Schauinsland, are very similar and probably tied to the distribution of human population. There is a tendency of an increase of the mean CH_4/CO_2 slopes from November to February (Table 2). At the same time, the $CO_2/^{222}$Radon slopes seem to be higher in November than during the subsequent months (December to February). The changing slope, therefore, can be attributed to a change of the CO_2 flux density. In fact, soil respiration CO_2 fluxes change from November (about 5 mmol CO_2 m^{-2} h^{-1}) to February (about 2 mmol CO_2 m^{-2} h^{-1}) by more than a factor of two (Dörr and Münnich, 1987), whereas the fossil fuel CO_2 flux changes not significantly throughout the winter months (Levin et al., 1995, Fig. 9).

As the CH_4 sources in western Europe are more than 95% anthropogenic (Thom et al., 1993) there is no reason to assume that the CH_4 emissions show a significant seasonality. However, we seem to observe significantly different slopes for $CH_4/^{222}Rn$ in the summer half year (18.3 ± 2.6 (ppb CH_4)/(Bq m^{-3} ^{222}Rn), mean $R^2 = 0.40$) than during the winter half year (24.4 ± 2.1 (ppb CH_4)/(Bq m^{-3} ^{222}Rn), mean $R^2 = 0.46$) (Table 2). This difference of about 25% could either point to a larger methane source density in winter than in the summer months if we assume constant ^{222}Radon flux throughout the year, or be caused by smaller ^{222}Radon emanations in the winter months where we have some evidence for (Dörr and Münnich, 1990; Schüßler, 1996). As is also obvious from Table 2, summer months with unique $CH_4/^{222}$Radon correlations over the whole month are rather sparse, and there is a tendency of smaller slopes being associated to smaller correlation coefficients. Looking at individual days, however, gives excellent correlation but the slopes of the individual regression lines vary from day to day. This is possibly the reason why we see no correlation in the monthly mean CH_4 offsets in summer (compare $\Delta CH_4/^{222}Rn$ scatter plot, Fig. 6d). The causes for these variable slopes are not yet fully understood. The generally good correlation between CO_2 and CH_4 throughout the winter (Figure 8 and Table 2) with only slightly variable slopes points to some poorly understood features in the ^{222}Radon concentrations. These may, however, also be associated to the fact that the measurements for CO_2 and CH_4 (UBA) have been made at a slightly different location than the measurements of ^{222}Radon (BfS).

The mean winter time slopes of $CH_4/^{222}$Radon and $CO_2/^{222}$Radon derived from half hourly values are 20–40% lower than the slopes derived from the monthly mean winter time offsets in section 3.2. (Fig. 6). This may point either to a smaller CH_4 and CO_2 source strength in the regional catchment area of the Schauinsland (e.g., the Rhine valley) or to slightly higher ^{222}Radon emissions in the regional surroundings of the Schauinsland. The slopes of the correlation between continental CO_2 and CH_4 offsets (6.5 ± 1.1 (ppb CH_4)/(ppm CO_2), $R^2 = 0.7$) respectively diurnal variations (7.8 ± 1.0 (ppb CH_4)/(ppm CO_2), $R^2 = 0.8$) in winter are the same within their uncertainty range, but significantly different from the slope Worthy et al. (1994) observed for polluted air masses arriving at Alert, Canada. The slopes these authors observe during episodes with air mass transports from Siberia during winter are between 9 and 16 (ppb CH_4)/(ppm CO_2) which corresponds to an about 50% higher CH_4 contribution from these areas with large natural gas emissions. Even larger slopes are observed by Conway and Steele (1989) at Point Barrow, Alaska (21 (ppb CH_4)/(ppm CO_2)), and in air from the higher Arctic troposphere (17.5 (ppb CH_4)/(ppm CO_2)) in spring 1986. However, the same authors observe a slope of 7.6 ± 0.7 (ppb CH_4)/(ppm CO_2) at Boulder, Colorado, during December 1985 which is close to what we measure for Schauinsland and the Rhine valley at Heidelberg (4.4 to 6.3 (ppb CH_4)/(ppm CO_2)), unpublished results from winter 1995–1996). A single diurnal cycle of CH_4 and CO_2 measured at the Jungfraujoch (47°N, 8°E, 3454m a.s.l.) high altitude background station in the Swiss Alps in December 1988 was 5.3 ± 0.9 (ppb CH_4)/(ppm CO_2), $R^2 = 0.67$, giving some idea about the ranges to be expected for the large scale European source mix.

3.4. Estimate of mean CO_2 and CH_4 flux densities

The regressions of mean ^{222}Radon activities with CO_2 and CH_4 offsets can be used to estimate mean flux densities of these two trace gases: We make the simplified assumption that the emanation rate of ^{222}Radon from soils is homogeneous in the catchment area of the Schauinsland station and constant with time, and we assume that the ^{222}Radon flux from ocean surfaces is negligible (Dörr and Münnich, 1990). If we, further, neglect radioactive decay of ^{222}Radon, the ^{222}Radon concentration of an air mass is almost proportional to its residence time over the continent (Levin et al., 1995). Neglecting radioactive decay of ^{222}Radon leads to underestimates of the residence time in the order of 20–30% (Thom et al., 1993).

Assuming that the sources of CO_2 and CH_4 are similarly homogeneously distributed like the ^{222}Radon sources then allows to estimate the CO_2 and CH_4 flux density (j_{CO_2,CH_4}) from respective concentration correlations, provided that the mean ^{222}Radon emanation rate from the soils is known ($j_{Rn}=(53\pm20)$ Bq m^{-2} h^{-1}; (Dörr and Münnich, 1990))

$$j_{CO_2,CH_4}=j_{Rn}\Delta c_{CO_2,CH_4}/c_{Rn}.$$

With the slopes ($\Delta c_{CO_2,CH_4}/c_{Rn}$) given in Figs 6b, c ($\Delta c_{CO_2}/c_{Rn}=4.8\pm0.6$ (ppm CO_2)/(Bq m^{-3} ^{222}Rn), $R^2=0.8$; $\Delta c_{CH_4}/c_{Rn}=27.9\pm7.2$ (ppb CH_4)/(Bq m^{-3} ^{222}Rn), $R^2=0.5$) we estimate a winter time flux density of $j_{CO_2}=10.4\pm4.3$ mmol m^{-2} h^{-1} and a methane flux density of $j_{CH_4}=0.066\pm0.034$ mmol m^{-2} h^{-1}. The CO_2 flux density of 10.4 mmol m^{-2} h^{-1} is about 50% larger than the mean flux density of anthropogenic CO_2 of about 7 mmol CO_2 m^{-2} h^{-1} estimated from statistical data for western Germany (Marland et al., 1994). The difference to the ^{222}Radon-derived flux density can be explained by biogenic emissions — mainly soil respiration during this time of the year. In fact, Dörr and Münnich (1987) reported direct flux densities for Germany from natural soils of about 3 mmol m^{-2} h^{-1} for the winter months (November to February). The mean winter time ^{222}Radon-derived methane flux density of 0.066 mmol CH_4 m^{-2} h^{-1} is also in very good agreement with statistical emission inventories, namely about 0.07 mmol CH_4 m^{-2} h^{-1} (Thom et al., 1993). These comparisons give us confidence in the method to derive mean trace gas emission rates from CO_2 and CH_4 concentration offsets and parallel ^{222}Radon observations.

The slopes from the regressions of diurnal concentration variations (Table 2) can be used in a equivalent way to estimate CO_2 and CH_4 flux densities in the regional catchment area of the Schauinsland station. The change in the winter time slopes of $CO_2/^{222}$Radon respectively $\Delta CO_2/^{222}$Radon have already been discussed. The significantly different $CH_4/^{222}$Radon slopes for summer and winter point to the possibility that indeed our assumption of a constant ^{222}Radon emanation rate all over the year may be uncorrect. It is well possible that the ^{222}Radon flux density from soils in the catchment area of the Schauinsland is smaller during winter due to higher soil humidity at that time of the year. It is, therefore, not totally clear if the smaller slopes during summer than during winter really indicate a smaller methane source in summer or if the ^{222}Radon approach is here on its quantitative limits. These variations have, however, to be investigated more thoroughly.

4. Conclusions

The combined interpretation of continuous CO_2, CH_4 and ^{222}Radon records provided insight into the causes of trace gas concentration variations at the continental mountain station Schauinsland. The large variations observed on the diurnal time scale for CH_4 and ^{222}Radon are due to convective transport of air to the mountain station which has been in close contact with regional ground level sources and sinks. During winter, all three gases are highly correlated, with the ratio of CH_4/CO_2 being very similar to values observed in other populated areas (Conway and Steele, 1989).

Using a mean value of the ^{222}Radon flux density from European soils, it was possible to estimate mean flux densities of CO_2 and CH_4 from the ratios of CO_2 respectively CH_4 and ^{222}Radon. These flux estimates were close to statistical estimates of mean emission inventories of anthropogenic sources and direct flux measurements for soil CO_2 emissions. It should be emphasized, however, that the uncertainty ranges of the ^{222}Radon-derived emission estimates have been calculated from averaging individual monthly results derived at one observational site only, and that the spatial variability of fluxes in Europe may be considerably larger. For methane, significantly different ratios to ^{222}Radon were observed in summer and winter which may possibly be due to a 25% lower ^{222}Radon emanation rate in the winter if compared to the summer half year.

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